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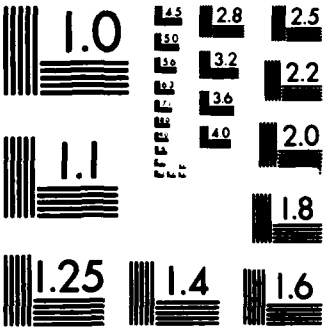

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Cure	Time-Temperature-Transformation (TTT)	
Thermal Degradation	Cure Diagram	
Gelation	Torsion Pendulum	

20 ABSTRACT (Continue on reverse side if necessary and identify by block number)

This Final Report summarizes experimental and theoretical results on relating cure to properties of thermosetting polymers.

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CURE AND PROPERTIES OF THERMOSETTING POLYMERS

FINAL REPORT

AUGUST 1987

U. S. ARMY RESEARCH OFFICE

CONTRACT NUMBER DAAG29-84-K-0037

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STATEMENT OF THE PROBLEM

Thermosetting materials (e.g., epoxies and polyimides) are used in composites, coatings and adhesives. Unlike their thermoplastic counterparts, molecular structure-macroscopic property relationships in thermosets are not well developed: hence the current research. A general model for thermosetting materials which relates polymerization to properties is being developed. In this, a time-temperature-transformation (TTT) cure diagram relates the principal states of matter encountered [i.e., liquid, rubber (sol/gel and gel), and glass (sol, sol/gel and gel)] to gelation and vitrification phenomena. The model is extended to rubber-modified thermosetting systems to show that a given chemical formulation can provide different morphologies and hence different material behavior. It is also extended to high temperature polymers where polymerization and degradation reactions compete. Computed and experimental TTT diagrams are compared. An automated dynamic mechanical technique for monitoring the cure and properties of thermosetting materials -- "torsional braid analysis" -- is the principal technique used.

SUMMARY OF THE MOST IMPORTANT RESULTS

Technical Report No. 1

Title: Time-Temperature-Transformation (TTT) Diagrams of High T_g Epoxy Systems: Competition Between Cure and Thermal Degradation

Abstract: The cure behavior and thermal degradation of high T_g epoxy systems have been investigated by comparing their isothermal time-temperature-transformation (TTT) diagrams. The formulations were prepared from di- and trifunctional epoxy resins, and their mixtures with stoichiometric amounts of a tetrafunctional aromatic diamine. The maximum glass transition temperatures ($T_{g\infty}$) were 229°C and > 324°C for the fully cured di- and trifunctional epoxy materials, respectively. Increasing functionality of the reactants decreases the times to gelation and to vitrification, and increases the difference between T_g after prolonged isothermal cure and the temperature of cure. At high temperatures, there is competition between cure and thermal degradation. The latter was characterized by two main processes which involved devitrification (decrease of modulus and T_g) and revitrification (char formation). The experimentally inaccessible $T_{g\infty}$ (352°C) for the trifunctional epoxy material was obtained by extrapolation from the values of $T_{g\infty}$ of the less highly crosslinked systems using a relationship between the glass transition temperature, crosslink density, and chemical structure.

Technical Report No. 2

Title: The Transformation of Liquid to Amorphous Solid: Effect of Reaction Mechanism on the Time to Vitrify for Linear and Network Polymerization

Abstract: A model is presented for the calculation of the time to vitrify of low molecular weight liquid on isothermal chemical reaction for linear- and network-forming polymerizations. For the linear case,

the model is based on the glass transition temperature (T_g) rising to the temperature of reaction (T_{cure}), and relationships between T_g and molecular weight, molecular weight and extent of reaction, and extent of reaction and time. For the nonlinear case, crosslink density is used instead of molecular weight. Step-growth and chain reaction mechanisms are considered. In a plot of T_{cure} versus time, the vitrification curve is generally S-shaped; the time passes through a maximum just above the glass transition temperature of the unreacted monomer(s) and passes through a minimum just below the glass transition temperature of the fully reacted material, which is in agreement with the limited available experimental data. The extent of reaction at vitrification is also presented. For the case of linear free-radical polymerization, existing free volume theory is also used to predict the extent of conversion at vitrification.

Technical Report No. 3
Title: Cure and Properties of Thermosetting Systems
Abstract: A generalized time-temperature-transformation cure diagram for thermosetting systems is discussed from the point of view of understanding relationships between cure, properties, and thermal degradation.

Technical Report No. 4
Title: Curing
Abstract: A generalized time-temperature-transformation cure diagram for thermosetting systems is discussed from the point of view of understanding relationships between cure, properties, and thermal degradation.

Technical Report No. 5
Title: Effect of Time-Temperature Path of Cure on the Water Absorption of High T_g Epoxy Resins
Abstract: The effect of different time-temperature paths of cure on the water absorption of high T_g epoxy resins has been investigated. The resins were cured isothermally for different times, with the following results: as extent of cure increased, the glass transition temperature (T_g) increased; the room temperature (RT) modulus decreased, the RT density decreased, the RT diffusion coefficient appeared to decrease, and the RT water absorption increased. The decrease in RT density is related to an increase in free volume, which controls the amount of water absorbed. A qualitative model accounts for the increase in RT free volume with increasing cure. The model is based on a restricted decrease of free volume on cure due to the rigid molecular segments in the cured resin systems. The sorption isotherms can be characterized by the dual mode theory at low activities but at high activities the sorption is complicated by penetrant clustering. A thermodynamic approach, independent of the absorption model, can correlate sorption data at different temperatures. The diglycidyl resin was also cured for extended times at three temperatures, in an effort to achieve full cure at each temperature. For these, the higher the cure temperature, the lower the RT density, which could result from the lower initial density of

materials cured at higher temperatures. The equilibrium water absorption increased with increasing cure temperature, consistent with the decrease in RT density. The systems studied were a diglycidyl ether of bisphenol A cured with an aromatic tetrafunctional diamine, trimethylene glycol di-p-aminobenzoate ($T_{g\infty}$ = 156°C), and a triglycidyl ether of tris(hydroxy phenyl)methane cured with the same amine ($T_{g\infty}$ = 268°C).

Technical Report No. 6
Title: Time-Temperature-Transformation (TTT) Cure Diagram of Thermosetting Polymeric Systems
Abstract: An isothermal time-temperature-transformation (TTT) cure diagram for thermosetting systems has been developed to aid in the understanding of the cure process and the properties after cure. The diagram summarizes in a convenient manner the temperature of cure (T_{cure}) vs. the times to gelation, vitrification, phase separation (in the case of rubber-modified systems), full cure, and thermal degradation. A more complete diagram could also include contours of constant conversion, viscosity, and modulus. The principal experimental technique which has been used to obtain a TTT diagram, torsional braid analysis (TBA), is described. Two recent models describing the cure process are reviewed; from these the time to vitrification vs. T_{cure} is computed from the chemical kinetics and the conversion at vitrification. One model uses a relationship between T_g and the extent of conversion at vitrification in conjunction with experimental data for the extent of conversion at vitrification, whereas the other predicts the extent of conversion at T_g from relationships in the literature. Both models predict an S-shaped time to vitrification curve, as has been obtained experimentally. The second model has been applied also to linearly polymerizing systems.

Technical Report No. 7
Title: Cure and Properties of Thermosetting Polymers
Abstract: This review discusses 1) the time-temperature-transformation cure diagram versus properties of thermosetting systems, 2) the torsional braid analysis and torsion pendulum methods for characterizing thermosetting systems, and 3) rubber-modified epoxies (their cure, transitions, morphology and mechanical properties).

LIST OF ALL PUBLICATIONS AND TECHNICAL REPORTS

Technical Report No. 1 December 1984
"Time-Temperature-Transformation (TTT) Diagrams of High T_g Epoxy Systems: Competition Between Cure and Thermal Degradation"
L. C. Chan, H. N. Naé and J. K. Gillham
Published in Journal of Applied Polymer Science, Vol. 29, pp. 3307-3327 (1984).

Technical Report No. 2 December 1984
"The Transformation of Liquid to Amorphous Solid: Effect of Reaction Mechanism on the Time to Vitrify for Linear and Network Polymerization"
M. T. Aronhime and J. K. Gillham
Published in Journal of Coatings Technology, Vol. 56, No. 718, pp. 35-47 (1984).

Technical Report No. 3 June 1985
"Cure and Properties of Thermosetting Systems"
J. K. Gillham
Published in British Polymer Journal, Vol. 17, No. 2, pp. 224-226 (1985).

Technical Report No. 4 March 1986
"Curing"
J. K. Gillham
Published in Encyclopedia of Polymer Science and Engineering, Second Edition, Vol. 4, pp. 519-524 (1986).

Technical Report No. 5 December 1986
"Effect of Time-Temperature Path of Cure on the Water Absorption of High T_g Epoxy Resins"
M. T. Aronhime, X. Peng, J. K. Gillham and R. D. Small
Published in Journal of Applied Polymer Science, Vol. 32, pp. 3589-3626 (1986). Ibid, Vol. 32, p. 6352 (1986).

Technical Report No. 6 December 1986
"The Time-Temperature-Transformation (TTT) Cure Diagram of Thermosetting Polymeric Systems"
M. T. Aronhime and J. K. Gillham
Published in Advances in Polymer Science, Vol. 78, pp. 83-113 (1986).

Technical Report No. 7 December 1986
"Cure and Properties of Thermosetting Polymers"
J. K. Gillham
Published in Structural Adhesives: Developments in Resins and Primers (Ed., A. J. Kinloch), pp. 1-27, 1986.

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